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ADVANCED MATERIALS

Supporting Information

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Band Gap Tunability in $Zn(Sn,Ge)N_2$ Semiconductor Alloys

Prineha Narang[1,3,†], Shiyou Chen[3,5,†], Naomi C. Coronel[1†], Sheraz Gul[4], Junko Yano[3,4], Lin-Wang Wang[3,5], Nathan S. Lewis[2,3] and Harry A. Atwater[1,3]

X-ray Absorption Fine Structure Spectroscopy Experimental Details

Curve fitting was performed with Artemis and IFEFFIT software using *ab initio*-calculated phases and amplitudes from the program FEFF 8.2. These *ab initio* phases and amplitudes were used in the EXAFS equation:

$$\chi(k) = S_0^2 \sum_j \frac{N_j}{kR_j^2} f_{eff_j}(\pi,k,R_j) e^{-2\sigma_j^2 k^2} e^{-2R_j/\lambda_j(k)} \sin(2kR_j + \varphi_{ij}(k)) \quad \text{(Equation S1)}$$

The neighboring atoms to the central atom(s) were divided into *j* shells, with all atoms with the same atomic number and distance from the central atom grouped into a single shell. Within each shell, the coordination number N_j denoted the number of neighboring atoms in shell *j* at a distance of R_j from the central atom. $f_{eff_j}(\pi,k,R_j)$ is the *ab initio* amplitude function for shell *j*, and the Debye-Waller term $e^{-2\sigma_j^2 k^2}$ accounted for damping due to static and thermal disorder in absorber-backscatterer distances. The mean free path term $e^{-2R_j/\lambda_j(k)}$ reflects losses due to inelastic scattering, where $\lambda_j(k)$ is the electron mean free path. The oscillations in the EXAFS spectrum are reflected in the sinusoidal term, $\sin(2kR_j + \varphi_{ij}(k))$ where $\varphi_{ij}(k)$ is the *ab initio* phase function for shell *j*. S_0^2 is an amplitude reduction factor due to shake-up/shake-off processes at the central atom(s). The EXAFS equation was used to fit the experimental data using *N*, *R*, and the EXAFS Debye-Waller factor (σ^2) as variable parameters. For conversion of the energy (eV) to wave vector (*k*, $Å^{-1}$) axis, E_0 was defined as 11111.0 eV and the S_0^2 value was fixed at 1.0. All fits were performed in the R space.

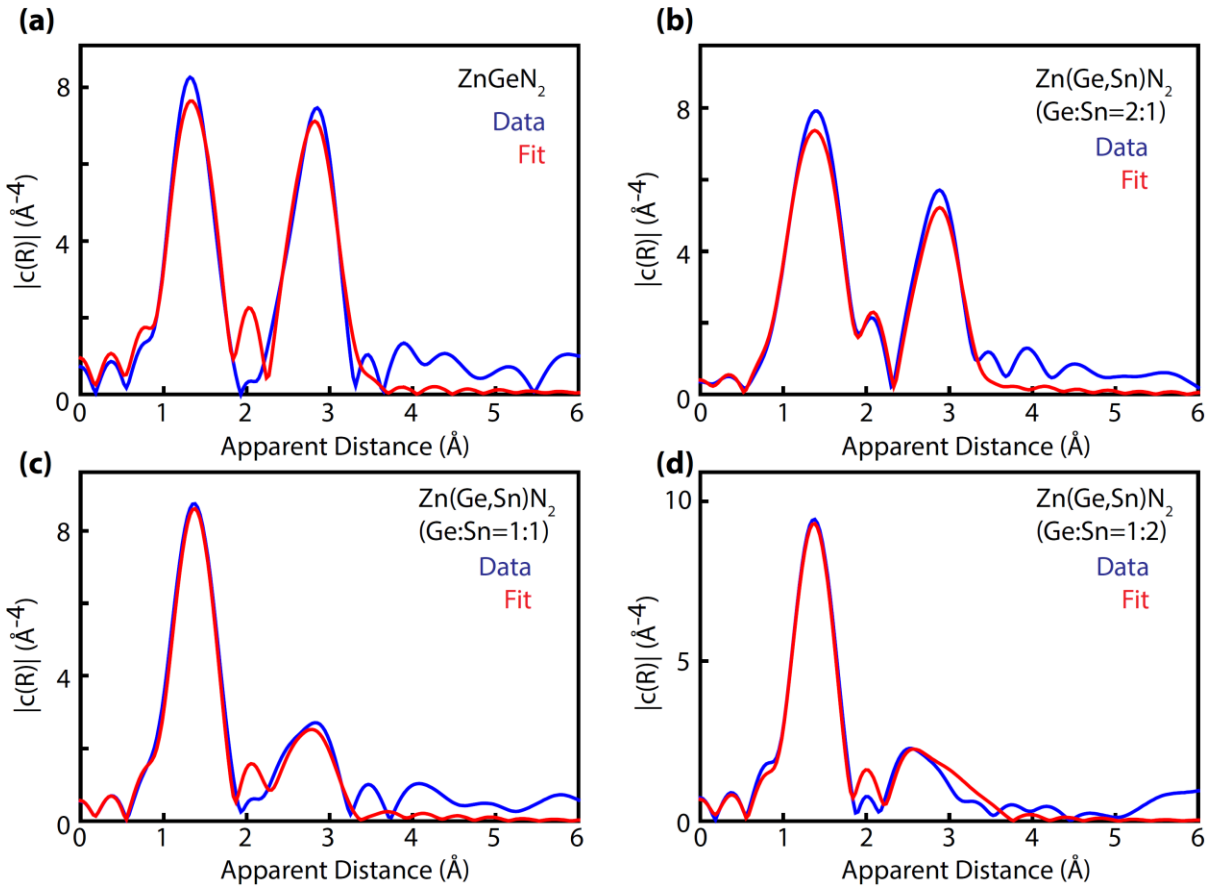

Figure S1: EXAFS curve-fitting results for $ZnSn_{1-x}Ge_xN_2$ alloys with the fitting parameters summarized in Table S1.

Table S1: Ge K-edge EXAFS curve fitting parameters.

	Path	R (Å)		N	σ^2 ($Å^2$)	R_f (%)
		EXAFS	XRD			
	Ge-N	1.86 (0.03)	1.84	**4.0**	0.004 (0.002)	2.7
$ZnGeN_2$	Ge-Zn	3.23 (0.08)	3.14	**8.0**	0.011 (0.001)	ΔE_0(eV)=2.3
	Ge-Ge	3.20 (0.04)	3.11–3.20	**4.0**	0.015 (0.005)	
	Ge-N	1.88 (0.09)		**4.0**	0.004 (0.008)	1.6
$ZnGeSnN_2$	Ge-Zn	3.26 (0.14)		**8.0**	0.012 (0.013)	ΔE_0=4.3
(Ge:Sn=2:1)	Ge-Ge	3.34 (0.01)		3.0	0.020 (0.001)	
	Ge-Sn	3.28 (0.60)		1.0	0.016 (0.020)	
	Ge-N	1.88 (0.08)		**4.0**	0.003 (0.007)	1.7
$ZnGeSnN_2$	Ge-Zn	3.28 (0.14)		**8.0**	0.020 (0.002)	ΔE_0=4.3
(Ge:Sn=1:1)	Ge-Ge	3.24 (0.10)		2.0	0.020 (0.001)	
	Ge-Sn	3.29 (0.44)		2.0	0.020 (0.003)	
	Ge-N	1.87 (0.12)		**4.0**	0.002 (0.011)	1.4
$ZnGeSnN_2$	Ge-Zn	3.29 (0.01)		**8.0**	0.020 (0.012)	ΔE_0=3.7
(Ge:Sn=1:2)	Ge-Ge	3.23 (0.01)		1.7	0.020 (0.012)	
	Ge-Sn	3.33 (0.30)		2.3	0.020 (0.002)	

N is the number of neighboring atoms, R, the atomic distance, σ^2, the Debye-Waller factor, and ΔE_0, the EXAFS threshold energy. Bold letters are the fixed parameters. The number in the parenthesis shows uncertainty in the variables. The goodness of the fit was evaluated by the EXAFS R-factor (R_f, %) that represents the absolute difference (least-square fit) between theory and data.

Special Quasi-random Structures of the $ZnSn_{1-x}Ge_xN_2$ alloys: The structural details of the SQS models used in our calculation are given in Table S2, with the corresponding atomic correlation functions listed in Table S3.

Table S2: Basis vectors (in Angstrom) and atomic coordinates (relative to the basis vectors) of the SQS used in our calculation for the $ZnSn_{1-x}Ge_xN_2$ alloys at concentration x=0.25, 0.50. For clarity, only the cation coordinates are shown.

x=0.50		x=0.25	
a	-6.72 -5.81 5.47	**a**	-6.72 -5.81 5.47
b	6.72 -5.81 5.47	**b**	6.72 -5.81 5.47
c	0.00 0.00 10.94	**c**	0.00 5.81 5.47
Zn	0.5000000 0.5000000 0.1875	Zn	1.09375000 0.09375000 0.1875000
Zn	0.1250000 0.3750000 0.1875	Zn	-0.15625000 0.09375000 0.4375000
Zn	1.0833335 0.5833335 0.4375	Zn	0.88541675 0.38541675 0.6041665
Zn	0.7083335 0.4583335 0.4375	Zn	0.63541675 0.38541675 0.8541665
Zn	1.0000000 0 0.1875	Zn	0.59375000 0.59375000 0.1875000
Zn	0.6250000 0.8750000 0.1875	Zn	0.34375000 0.59375000 0.4375000
Zn	0.5833335 0.0833335 0.4375	Zn	0.38541675 0.88541675 0.6041665
Zn	0.2083335 0.9583335 0.4375	Zn	0.13541675 0.88541675 0.8541665
Zn	0.5000000 0.5000000 0.6875	Zn	0.34375000 0.34375000 0.6875000
Zn	0.1250000 0.3750000 0.6875	Zn	0.09375000 0.34375000 -0.0625000
Zn	1.0833335 0.5833335 0.9375	Zn	1.13541675 0.63541675 1.1041665
Zn	0.7083335 0.4583335 0.9375	Zn	-0.11458325 0.63541675 0.3541665
Zn	1.0000000 0 0.6875	Zn	0.84375000 -0.15625000 0.6875000
Zn	0.6250000 0.8750000 0.6875	Zn	0.59375000 0.84375000 -0.0625000
Zn	0.5833335 0.0833335 0.9375	Zn	0.63541675 0.13541675 1.1041665
Zn	0.2083335 0.9583335 0.9375	Zn	0.38541675 1.13541675 0.3541665

Sn	0.2500000 0.7500000 0.1875	Sn	0.84375000 0.34375000 0.1875000
Sn	0.3333335 0.3333335 0.4375	Sn	0.13541675 0.13541675 0.6041665
Sn	0.8750000 0.6250000 0.1875	Sn	0.59375000 0.34375000 0.4375000
Sn	0.9583335 0.2083335 0.4375	Sn	0.88541675 0.13541675 0.8541665
Sn	0.3750000 0.1250000 0.1875	Sn	0.34375000 0.84375000 0.1875000
Sn	0.4583335 0.7083335 0.4375	Sn	0.63541675 0.63541675 0.6041665
Sn	0.2500000 0.7500000 0.6875	Sn	0.38541675 0.63541675 0.8541665
Sn	0.3333335 0.3333335 0.9375	Sn	0.09375000 0.59375000 0.6875000
Ge	0.7500000 0.2500000 0.1875	Sn	0.38541675 0.38541675 0.1041665
Ge	0.8333335 0.8333335 0.4375	Sn	0.84375000 0.59375000 0.9375000
Ge	0.8750000 0.6250000 0.6875	Sn	0.13541675 0.38541675 0.3541665
Ge	0.9583335 0.2083335 0.9375	Sn	0.59375000 0.09375000 0.6875000
Ge	0.7500000 0.2500000 0.6875	Ge	0.09375000 0.84375000 0.4375000
Ge	0.8333335 0.8333335 0.9375	Ge	0.88541675 0.88541675 0.1041665
Ge	0.3750000 0.1250000 0.6875	Ge	0.34375000 0.09375000 0.9375000
Ge	0.4583335 0.7083335 0.9375	Ge	0.63541675 0.88541675 0.3541665

Table S3: Atomic correlation functions for the atomic clusters (*k,m)* with *k* vertices and up to the *m*-th neighbor of the SQS used in our calculation, at the alloy concentration *x*=0.25, 0.5, and compared with the ideal values of the random alloy.

(m,k)	(2,1)	(2,2)	(2,3)	(2,4)	(3,2)	(3,3)	(3,4)	(4,3)	(4,4)
***x*=0.50**									
Random	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
SQS	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-1.0
***x*=0.25**									
Random	0.25	0.25	0.25	0.25	-	0.125	0.125	0.0625	0.0625
SQS	0.25	0.25	0.25	0.25	-	0.000	0.250	0.0000	0.2500

Calculated density of states of $ZnSnN_2$ and $ZnGeN_2$: The calculated density of states for $ZnSnN_2$ and $ZnGeN_2$ is given in Figure S2, with the energy relative to the valence band maximum (VBM) eigen-energy.

Figure S2: Calculated total and partial density of states of (a) $ZnSnN_2$ and (b) $ZnGeN_2$. The partial density of states is projected on Zn, Sn, Ge and N s, p, and d orbitals respectively.